

Charge inversion in colloidal systems

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Abstract

We investigate spherical macroions in the strong Coulomb coupling regime within the primitive model in salt-free environment. Molecular dynamics (MD) simulations are used to elucidate the effect of *discrete* macroion charge distribution on charge inversion. A systematic comparison is made with the charge inversion obtained in the conventional continuous charge distribution. Furthermore the effect of multivalent counterions is reported.

Key words: charged colloids, charge inversion, molecular dynamics

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1 Introduction

Charged colloids (macroions) might exhibit very surprising behaviors due to the Coulomb interaction and the two different length scales involved there: (i) microscopic (counterions) and (ii) mesoscopic (macroions). A very spectacular effect which has attracted great attention these last years is the phenomenon of overcharging [1–8]. This situation occurs when the number of counterions in the vicinity of the macroion surface is so high that the macro-particle bare charge is overcompensated (charge inversion). This phenomenon has been observed experimentally by electrophoresis [9,10]. On the theoretical side, a massive effort has been recently devoted to elucidate this striking phenomenon. Wigner crystal theories have been successfully applied to understand charge inversion [1,3–6,8] and quantitative agreement was found with simulations [8].

It turns out that all numerical and analytical methods, undertaken so far, neglect the *discrete* nature of the macroion charge distribution. But in realistic systems the macroion charge is not continuously distributed over the macro-particle, but rather carried by small microscopic ions. It is only very recently that a simulation study has been reported where the macroion charge discreteness has been considered [7].

In this paper, we concentrate on the effect of the macroion charge distribution discreteness. In particular, we study this effect on the overcharging properties. Besides we show that it is possible to have stronger overcharge in the discrete case than in the continuous case.

2 Computational details

2.1 Macroion charge discretization

The procedure is similar to the one used in a previous study [7]. The macroion charge discretization is produced by using Z_m *monovalent* microions of diameter σ distributed *randomly* on the surface of the macroion (see Fig. 1). Then the macroion structural charge is $Q = -Z_m e$ [11] where $Z_m > 0$ and e is the positive elementary charge. The counterions have a charge $q = +Z_c e$ where $Z_c > 0$ stands for the counterion valence. The discrete colloidal charges (DCC) are *fixed* on the surface of the spherical macroion and are at a distance r_0 from the macroion center. Thus to produce a random discrete charge distribution on the surface we generated (uniformly) randomly the variables $\cos \theta$ and φ where θ and φ are the standard spherical angle coordinates. Excluded volume is taken into account by rejecting configurations leading to an overlap of microions. Phenomena such as surface chemical reactions [12], hydration, roughness [13] are not considered.

2.2 Molecular dynamics procedure

A MD simulation technique was used to compute the motion of the counterions coupled to a heat bath acting through a weak stochastic force $\mathbf{W}(t)$. The motion of counterion i obeys

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i U(\mathbf{r}_i) - m\gamma \frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t), \quad (1)$$

where m is the counterion mass, U is the potential force having two contributions: (i) the Coulomb interaction and (ii) the excluded volume interaction, and γ is the friction coefficient. Friction and stochastic force are linked by the dissipation-fluctuation theorem $\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6m\gamma k_B T \delta_{ij} \delta(t - t')$. For the ground state simulations the stochastic force is set to zero.

Excluded volume interactions are taken into account with a pure repulsive Lennard-Jones potential given by

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r - r_0} \right)^{12} - \left(\frac{\sigma}{r - r_0} \right)^6 \right] + \epsilon, \quad (2)$$

if $r - r_0 < r_{cut}$, and $U_{LJ}(r) = 0$ otherwise. For the microion-microion interaction (the microion being either a counterion and/or a DCC), whereas $r_0 = 7\sigma$ for the macroion-counterion interaction, and $r_{cut} = 2^{1/6}\sigma$ is the cutoff radius. This leads to a macroion-counterion distance of closest approach $a = 8\sigma$.

Energy and length units in our simulations are related to experimental units by taking $\epsilon = k_B T_0$ (with $T_0 = 298$ K), and $\sigma = 3.57$ Å respectively.

The pair electrostatic interaction between any pair ij , where i and j denote either a DCC, a counterion or the central charge (for the case of the continuous surface charge distribution), reads

$$U_{coul}(r) = k_B T_0 l_B \frac{Z_i Z_j}{r}, \quad (3)$$

where $l_B = e^2 / 4\pi\epsilon_0\epsilon_r k_B T_0$ is the Bjerrum length (here $l_B = 10\sigma$) describing the electrostatic strength.

The macroion and the counterions are confined in a spherical impenetrable cell. The macroion is held fixed and is located at the center of the cell. To avoid image charge complications, the permittivity ϵ_r is supposed to be identical within the whole cell (including the macroion) as well as outside the cell.

3 Results

The simplest way to quantify overcharging in salt-free environment is to compute the total electrostatic energy of the system in the *ground state* (i. e., $T = 0$ K) as a function of the number of overcharging counterions n . Although this approach is very idealized, it allows an insight into the mechanisms governing overcharging.

In what follows we are going to compare systematically (for a macroion charge $Z_m = 60$) the overcharging occurring in the continuous case (CC), as is conventionally done, and in the discrete case (with DCC ions). Fig. 1 shows a typical starting equilibrium configuration with a discrete macroion charge distribution where the system is globally neutral (before adding excess overcharging counterions).

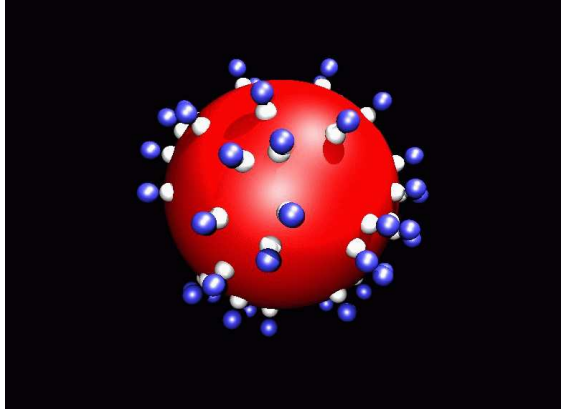


Fig. 1. Ground state structure for a discrete macroion charge distribution with $Z_m = 60$. The monovalent discrete colloidal charges are in white and the monovalent counterions (here $Z_c = 1$) in blue. Full ionic pairing occurs.

Fig. 2(a) shows overcharging energy profiles for $Z_m = 60$ and *monovalent* counterions ($Z_c = 1$). It is observed that overcharging is stronger in the continuous case than in the discrete case as one could expect. More precisely the gain in energy as well as the maximal number of stabilizing overcharging counterions (corresponding to a minimum in the $E - n$ curve) are higher when the surface macroion charge is continuous. Indeed, having in mind that overcharging is enhanced by counterion ordering, it is clear that in the discrete case where strong ionic pairing occurs (between DCC site and counterion - see Fig. 1) the counterion ordering is lowered and thus leads to a weaker charge inversion. However since overcharging occurs in the discrete case, the excess counterions still experience an attractive interaction with their neighboring dipoles (ionic pairs). This ion-dipole interaction is the driving force for the overcharging in the discrete case with monovalent counterions. Nevertheless it has been shown elsewhere [7] that by decreasing the mean separation between DCC sites (i. e., increasing macroion charge density) the difference in overcharging between discrete and continuous macroion charge distribution decreases.

When we consider *multivalent* counterions the situation is qualitatively different. Indeed, one observes that for $Z_c = 2$ and 3 overcharging is even stronger in the discrete case [see Figs. 2 (b-c)]. This is a rather counter-intuitive phenomenon, since ionic pairing is still effective. The crucial difference between monovalent and multivalent counterion systems is that overcharging occurs with ionic pairing for multivalent counterions (since free monovalent DCC sites are unbound), whereas for monovalent counterions only ion-dipole interaction can take place (since in the neutral state *each* DCC site is already bound with a monovalent counterion). Obviously for these systems under consideration depicted in Figs. 2 (b-c), the ionic pairing energy is a fundamental quantity that controls the overcharging strength. More precisely, the stronger the ionic bonding the more efficiently it overcomes the *excess* overcharge "self-energy",

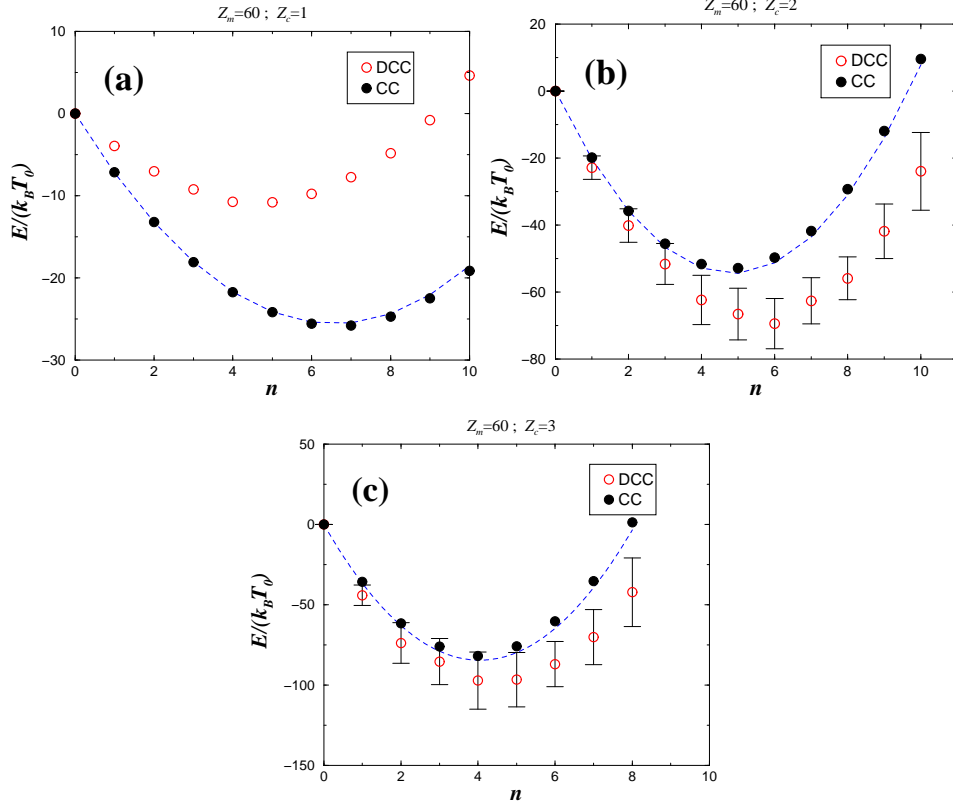


Fig. 2. Total electrostatic energy for ground state configurations (with $Z_m = 60$) as a function of the number of *overcharging* counterions n : (a) $Z_c = 1$ (b) $Z_c = 2$ (c) $Z_c = 3$. Overcharge curves were computed for discrete macroion charge distribution (DCC) and central macroionic charge (CC). The neutral case was chosen as the potential energy origin. Dashed lines were produced by using Wigner Crystal theory [8]. For discrete systems (DCC) error bars are only indicated when larger than symbols.

and therefore the higher the overcharging for multivalent counterion systems.

Beside of the ionic bonding strength there is another important parameter controlling overcharging: the surface macroion charge density. When the macroion charge density is high enough (not reported here) then the $E(n)$ curves become quasi-identical for discrete and continuous charge distributions. In terms of length scales, the relevant parameter controlling charge reversal with discrete distribution is the ration ρ between the mean distance between DCC and the distance separation of the ionic pair. For low ρ the effects of discretization are very important whereas for $\rho \rightarrow 1$ one recovers the continuous limit.

4 Conclusions

We carried out MD simulations to elucidate the effect of discrete macroion charge distribution on the overcharging. We showed that overcharging is still effective in the discrete case. For multivalent counterions and a sufficiently low macroion charge density, overcharging can even be stronger in the discrete case than in the continuous case. Future works will address aqueous solutions at finite temperature as well as the presence of salt-ions.

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